A simple scaling law between the total energy of a free atom and its atomic number

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A simple, approximate relation is found between the total energy of a free atom and its atomic number: $E \simeq -Z^{2.411}$. The existence of this index is inherent in the Coulomb and many-body nature of the electron-electron interaction in the atomic system and cannot be fabricated from the existing fundamental physical constants.

In a recent work on the calculation of the cohesive energy of elemental crystals, [1] we have calculated the total energy for all atoms with Z≤92. Our calculations were based on the density functional theory with the local density approximation. [2] Parameterization of the exchange-correlation interaction is that of Hedin-Lundqvist. [3] For the first time, we plotted the total energy (E) versus the atomic number (Z) curve (Fig. 1), in an attempt to gain some physical insight into the density functional theory. Surprisingly, it is found that this curve can be very well fitted by a scaling law

$$E = -Z^n, \quad n = 2.411$$

To make the $E \sim Z$ relation more illustrative, the $n \sim Z$ curve is plotted in Fig. 2 (down triangles)). The power index n is almost constant (close to 2.41) for atoms with $4 \leq Z \leq 92$. If there is no interaction between electrons, $n = 3$; and if there is only one electron outside this nucleus, $n = 2$. Since the electron-electron interaction increases the total energy (i.e., less negative), n should meet $2 < n < 3$. The existence of such a near-constant power index is astounding because, due to the complexity of the quantum many-body problem, it's never been expected that the total energy of an atom other than hydrogen should have so simple a relation with its atomic number.

Exceptions occur in the cases of hydrgen, helium, and lithium. For hydrogen, $Z = 1$ and $E = -0.976 \ Ry$, therefore, n has no definite value. For helium and lithium, n=2.506 and 2.447, respectively, apparently larger than 2.41. Experimental data [4], which is non-relativistic and available up to argon, are denoted by triangles in Fig.2. Also listed are the calculated power index from Desclaux's Hartree-Fock atomic total energy data. [5] Open circles represent non-relativistic treatment and solid circles denote relativistic treatment. It is seen that all these four groups of n have values with very limited diviation. It's then concluded that the scaling law is not an outcome of the density functional theory, where both the exchange and correlation interactions are considered, nor a result of the Hartree-Fock approximation, in which only the exchange interaction is counted. Although relativistic effects makea difference in the index n, the approximate scaling law holds for both cases.

As ionization potentials show very strong effects of chemical periodicity, it is of much interest to see whether they exert a periodic effect on the atomic total energy too. We replot the $n \sim Z$ curves in Fig.3, a higher resolution graph. n shows apparent oscillatory behavior for atoms lighter than krypton. But for heavier atoms, it displays monotonic character. This is due to the fact that the ionization potentials are so small as to be averaged out for the heavy atoms. It is worth noting that the solid circle denoting Desclaux's relativistic francium falls out of the otherwise smooth curve. There must be an abrupt mistake, probably a typo, in the reported total atomic total energy of francium.

From the comparisons between density functional theory and Hartree-Fock approximation, relativistic and non-relativistic treatments, we can conclude that the existence of such a simple relation between the total energy of an atom and its atomic number is independent of the framework in which the calculations of atomic total energy are carried out. It is inherent in the Coulomb and many-body nature of the atomic system. Apparently, this power index cannot be fabricated from the existent fundamental physical constants such as $\hbar$, c, e, etc., and can only be built into a new many-body quantum theory.

ACKNOWLEDGMENTS

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[4] R. C. Weast, Ed., CRC Handbook of Chemistry and Physics, 58th ed., Chemical Rubber Co., Cleverland, 1977.
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FIG. 1. Atomic total energy (Ry) given by density functional theory.

FIG. 2. Calculated power index n in relation $E = -Z^n$. Down triangles are our results from density functional theory; open (non-relativistic) and solid (relativistic) circles are calculated from Desclaux's Hartree-Fock data; triangles denote experimental data (non-relativistic).
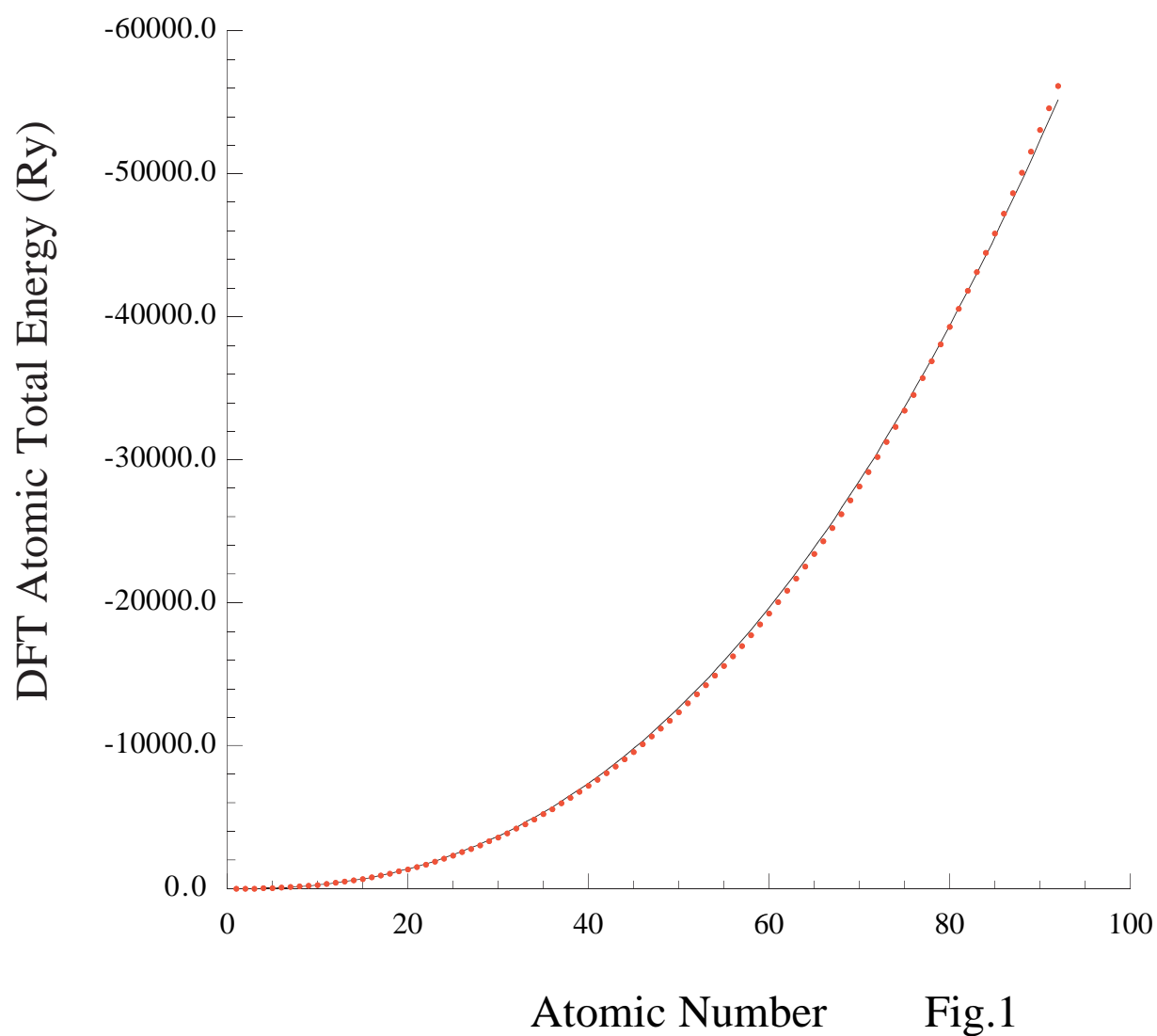
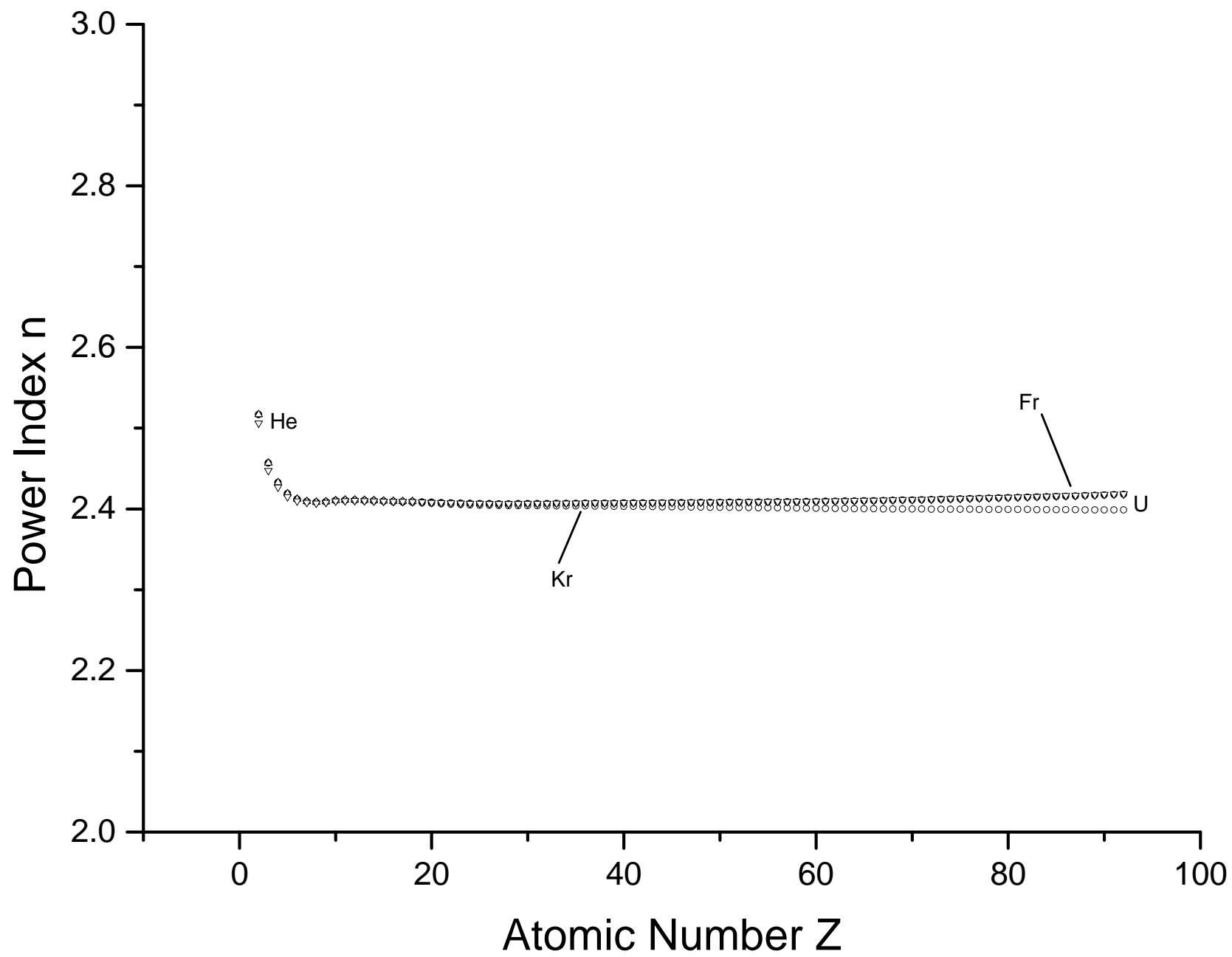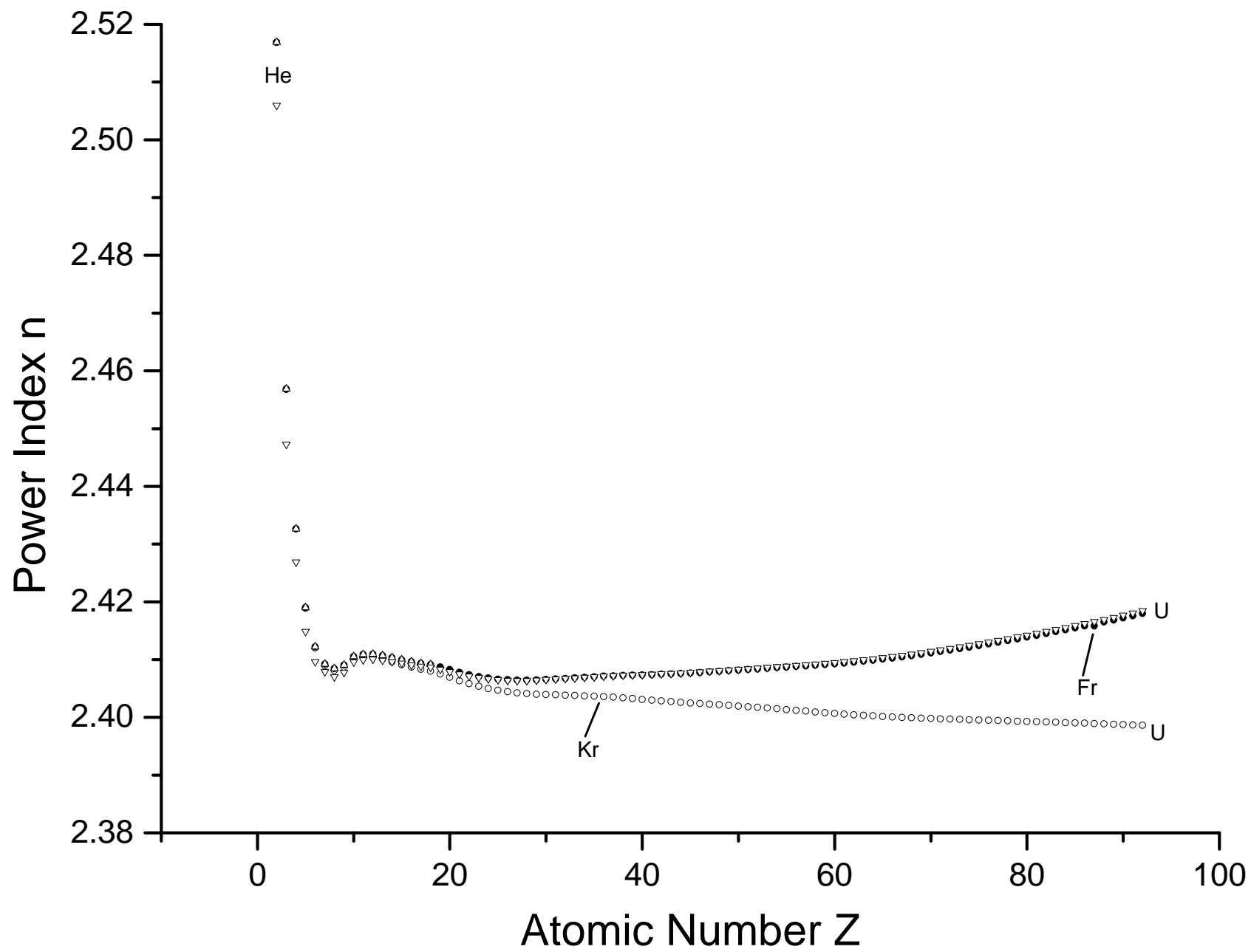FIG. 3. A replot of Fig.2 with higher resolution.

Fig.1

Fig.2

Fig.3